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(54) **Ziegler type catalyst system.**

(57) A Ziegler type catalyst system for alpha-olefin type polymerization which includes R'_3Y, R'_2YX or a mixture thereof, at least one supported Group IVA–VIII transition metal halide and an alkyl metal compound selected from R'_2YNR_2 and $R'XYNR_2$, wherein Y is Al, Ga or In. The improved catalyst system provides increased polymerization activity without significantly affecting the crystallinity of the polymer.

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The present invention relates to improved Ziegler type catalyst systems for the conventional alpha-olefin type polymerizations thereby yielding polymers having a high degree of isotactic stereoregularity.

An object of the present invention is to provide improved Ziegler type catalyst systems having a major increase in polymerization activity while being able to control the polymer crystallinity over a wide range, e.g., isotacticity, wherein the catalyst system includes at least one Group IVA-VIII transition metal halide, an alkyl metal cocatalyst selected from the group consisting of R'_3Y or R'_2YX and mixtures thereof and an alkyl metal compound being selected from R'_2YNR and $R'XYNR_2$, wherein R' is selected from the group consisting of C_1 to C_{20} primary alkyl, secondary alkyl, tertiary alkyl, neopentyl alkyl, branched alkyl, naphtenic, or aralkyl groups, X is a halide group, R is selected from the group consisting of C_3 to C_{20} bulky alkyl groups, cycloalkyl groups, aryl groups, or a cyclic amine structure, and Y is selected from the group consisting of aluminum, gallium and indium.

A further object of the present invention is to provide an improved process for alpha-olefin type polymerizations, wherein the polymerization activity is increased without adversely affecting the crystallinity of the formed polymer.

A still further object of the present invention is to provide an improved Ziegler type catalyst system wherein catalyst poisons are consumed in situ thereby minimizing the

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formation of atactic type polymers wherein the catalyst poison $R'AlX_2$ is effectively removed from the catalyst thereby making a higher number of active sites.

A still further object is the advantage over the alternative catalysts of being able to use the present compounds directly with any type of transition metal halide without modification of the commercial catalyst preparation or the polymerization plant.

During a Ziegler type alpha-olefin polymerization which employs $TiCl_3$ in combination with R'_3Y or R'_2YX, the by-product $R'YX_2$ is formed on the surface of the $TiCl_3$ thereby acting as a catalyst poison (deactivator), wherein R' is selected from the group consisting of C_1 to C_{20} primary alkyl, secondary alkyl, tertiary alkyl, neopentyl alkyl, branched alkyl, naphthenic or aralkyl groups, preferably a C_2 to C_4 alkyl group, X is a halide group, Y is selected from the group consisting of Al, Ga or In.

It has been shown that the addition of small amounts of $EtAlCl_2$ to a $TiCl_3$-Et_2AlCl catalyst system dramatically reduces polymerization rates (Ingberman, et. al., J. Polymer Sci. A4, 2781 (1966)). Since the formation of an active catalyst site during polymerization involves the reaction $R'_2AlCl + TiCl_3 \longrightarrow R'AlCl_2 + R'TiCl_2$ on the surface of the $TiCl_3$ crystal, it is apparent that the $R'AlCl_2$ catalyst poison (or deactivator) is always present in such catalyst systems.

Likewise for the reaction of R'_3Al with excess $TiCl_3$ is:

$$R'_3Al + TiCl_3 \text{ (excess)} \rightarrow R'AlCl_2 + R'_2AlCl + 3R'TiCl_2(TiCl_3)x$$

It has been surprisingly found that this catalyst poison $R'AlX_2$ can be effectively removed from the surface of the $TiCl_3$ by the addition of a compound R'_2YNR_2 or $R'XYNR_2$ to the $TiCl_3$-R'_3Al or $TiCl_3$-R'_2AlX. The R'_2YNR_2 reacts selectively with $R'AlX_2$ in two different ways either to remove the $R'AlX_2$ by the formation of mixed dimers:

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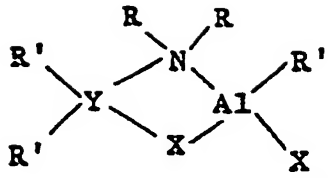
$$(R'_2YNR_2)_2 + (RAlX_2)_2 \longrightarrow 2$$ 

or by transalkylation to regenerate R'_2AlX and to generate $R'XYNR_2$: $R'_2YNR_2 + R'AlX_2 \longrightarrow R'XYNR_2 + R'_2AlX$. In the case of $R'XYNR_2$, the $R'AlX_2$ is simply removed by formation of a catalytically inactive mixed dimer. In either case, the $R'AlX_2$ is effectively removed from the catalyst sites, thereby resulting in a higher number of active sites per unit of catalyst volume which is reflected in a large increase in activity. When the amide (R'_2YNR_2) of the present invention is used in relatively small amounts based on the R'_3Al or R'_2AlX, the polymer isotacticity (as measured by heptane insolubles, density, tensile, etc.) is similar to or higher than that obtained with either R'_3Al or R'_2AlX alone. When higher proportions are used relative to R'_2AlX or R'_3Al, the polymer becomes less isotactic, but polymerization rates increase to even higher levels. Thus, one can achieve remarkable increases in activity from any $TiCl_3$ or $TiCl_4$ catalyst while simultaneously controlling polymer isotacticity over a wide range. Another advantage the cocatalyst supplement of the invention has over alternative catalysts is that it may be used directly with any type of $TiCl_3$ or $TiCl_4$ presently being used without modification of the commercial catalyst preparation or the polymerization plant.

The amides usable in the invention have the general structures R'_2AlNR_2 and $R'XAlNR_2$, wherein R' = C_1 to C_{20} hydrocarbyl group such as primary alkyl, secondary alkyl, tertiary alkyl, neopentyl alkyl, branched alkyl, cycloalkyl, or aralkyl, preferably a C_{1-12} alkyl; and R = C_3 to C_{20} bulky alkyl, cycloalkyl, aryl or substituted aryl groups, including ring structures such as R_2Al piperidide and Et_2Al pyrrolidide. Hindered amide groups derived from hindered secondary amines are especially preferred because they interact less strongly with the $TiCl_3$ and have greater driving

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force to form mixed dimers with the $R'AlCl_2$ poison. Such compounds have large, bulky R groups by virtue of branching on the carbons alpha, beta or gamma to the nitrogen. Illustrative examples of R groups include isopropyl, isobutyl, neopentyl, 3,3-diethylhexyl, 2-ethylhexyl, 2-butyl, 2-octyl, 3-pentyl, cyclohexyl, cyclopentyl, 2-methyl-cyclopentyl, 3-ethycyclohexyl, phenyl, totyl, xylyl, chlorophenyl, naphthyl and mixtures including mixtures in which one R group may be a less bulky saturated group such as a normal alkyl. Also, the two R groups may be part of a cyclic amine structure, such as pyrrolidyl, piperidyl, and the like and their various alkyl substituted derivatives especially when the substituents are on the carbon atoms adjacent to the nitrogen atoms, such as 2,6-diisopropylpiperidide, 2,2,6,6-tetramethylpiperidide, and the like.

The Y group of R'_2YNR_2 is selected from the group consisting of aluminum, gallium, or indium, most preferably aluminum.

The ratio of amide to $TiCl_3$ is between 0.05:1 to 5:1. The lower ratios are used together with "low aluminum" containing $TiCl_3$ to make highly isotactic polymers at high rates. Higher ratios are used with aluminum-containing $TiCl_3$ catalysts such as the commercial $TiCl_3 \cdot 0.33\ AlCl_3$ catalyst. "Low-aluminum" containing $TiCl_3$ refers to $TiCl_3$ catalysts which have low Al because of method of formation or have had a major portion of the aluminum removed as a result of subsequent reactions.

These new cocatalyst mixtures are useful with any of the crystal modifications of TiX_3, with solid solutions of Groups II-III metal salts in TiX_3 (also referred to as "co-crystallized" such as $TiCl_3 \cdot nAlCl_3$ or $TiCl_3 \cdot nMgCl_2$, and with TiX_3 or TiX_4 supported on salts such as $MgCl_2$ or hydroxychloride, oxides or other inorganic or organic supports, wherein X = Cl or Br, preferably Cl. Lewis bases, alcohols, carboxylic acids, etc. may also be present. The most preferred crystal structure is delta or pseudo delta, the latter being a mixture of disordered, very small alpha and gamma

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crystallites. This invention is also useful for increasing the activity and/or stereo-specificity of supported $TiCl_4$ and $TiCl_3$-type catalysts and other supported predominantly trivalent titanium compounds. The $TiCl_3$-type catalysts may be prepared from $TiCl_4$ by any of the reduction and crystallization procedures known in the art (H_2, metal metal hydrides, alkyl, etc.). Low aluminum $TiCl_3$ type catalysts are preferred.

Lewis bases can be employed in combination with the trialkyl metal compound or with the Group IVA to VIII transition metal compound or with both components as long as they do not cause excessive cleavage of metal-carbon bonds or loss of active sites. A wide variety of Lewis bases may be used including such types as tertiary amines, esters, phosphines, phosphine oxides, phosphates (alkyl, aryl), phosphites, hexaalkyl phosphoric triamides, dimethyl sulfoxide, dimethyl formamide, secondary amines, ethers, epoxides, ketones, saturated and unsaturated heterocycles, or cyclic ethers and mixtures thereof. Typical but non-limiting examples are diethyl ether, dibutyl ether, tetrahydrofuran, ethylacetate, methyl p-toluate, ethyl p-anisate, ethyl benzoate, phenyl acetate, amyl acetate, methyl octanoate, acetophenone, benzophenone, triethylamine, tributyl amine, dimethyldecylamine, pyridine, N-methylpiperidine, 2,2,6,6-tetramethylpiperidine, and the like. Especially useful in combination with the trialkyl metal cocatalyst are Lewis bases whose complexing ability toward the cocatalyst is "hindered" sufficiently by steric and/or electronic effects to cause appreciable dissociation of the trialkyl metal-Lewis base complex under polymerization conditions. Although a wide range of mole ratios may be used, dissociation of the complex as measured on a 1:1 complex is normally in the range of 1-99 mole %, more preferably 5-95%, and most preferably greater than 10% and less than 90%. Steric hindrance is achieved by bulky substituents around the heteroatom which reduces the accessibility of the base functionality to the Lewis acid, that is, the trialkyl metal compound. Electronic hindering is obtained by placing electron withdrawing sub-

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stituents on the heteroatom to reduce the electron density on basic heteroatom. Aromatic substituents are especially useful because they are relatively unreactive toward other catalyst components. Hindered Lewis bases derived from piperidines, pyrrolidines, ketones, tetrahydrofurans, secondary and tertiary aromatic amines and tertiary aliphatic amines are preferred, with the hindered nitrogen bases being most preferred. Non-limiting examples of sterically hindered bases include 2,2,6,6-tetramethylpiperidine, 2,2,5,5,-tetramethylpyrrolidine, 2,2,5,5,-tetramethyltetrahydrofuran, di-tert-butylketone, 2,6-diisopropylpiperidine, ortho-tolyl t-butyl ketone, methyl 2,6-di-tert-butylphenylketone, diisopropylethylamine,t-butyldimethylamine, 6-methyl-2-isopropylpyridine, and the like. Electronically hindered Lewis bases include diphenylamine, di-ortho-tolylamine, N,N-diethyl-aniline, di-ortho-tolylketone, and the like. Since aromatic substituents are also bulky, some of the electronically hindered bases can also have a steric contribution to the hindrance. Especially preferred hindered amines are 2,2,6,6-tetramethylpiperidine, 2,2,5,5,-tetramethyl-pyrrolidine and the diarylamines. Completely hindered bases, such as 2,6-di-tertiarybutylpyridine, and the like, which complex the alkyl metal cocatalyst too weakly, are ineffective for improving sterospecificity and are excluded from this invention.

Further increases in activity or stereospecificity may be obtained by premixing the transition metal component with either the amide or the alkyl metal, or both.

The amide effect is obtained with all the usual polymerization conditions. Thus solvent, temperature and monomer concentrations are not critical. Increased activity is obtained with all alpha olefins from ethylene to C_{10} and higher as well as in copolymerizations such as ethylene/α-olefin, ethylene/diolefin, propylene/α-olefin, propylene/diolefin and ethylene/α-olefin/diene copolymerizations. The amount of alkyl metal cocatalyst is usually in the range of 0.1:1 to 20:1, preferably 0.5:1 to 10:1 mole ratio of

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alkyl metal to transition metal compound. It is feasible using the hindered amides and hindered Lewis bases to employ higher mole ratios, up to 200:1 or higher, to achieve higher activity at high stereospecificity. The most preferred mole ratios with the hindered components is in the range 5:1 to 200:1 alkyl metal plus amide to transition metal compound.

The concept of the invention can be restated as follows. Two types of alkyl metal compounds have been found to be effective for greatly increasing the activity of Ziegler catalysts, especially for propylene polymerization. These are alkyl aluminum dialkylamides and alkyl chloroaluminum dialkyl amides. The amides most preferably are sterically hindered. Both types are believed to operate by selectively scavenging the $R'AlCl_2$ poison from the catalyst through the formation of mixed dimers. The dialkylaluminum additives are preferred because they regenerate the desirable R_2AlCl by reaction with $RAlCl_2$. However, the corresponding alkyl chloroaluminum amides are also effective additives for simply scavenging $RAlCl_2$. These latter have the advantage over the dialkylaluminum types in that they have little, if any, polymerization activity so that the amounts used need not be so carefully controlled.

When the dialkylaluminum amide additives are used in excess over the amount of $R'AlCl_2$ produced by the catalyst reactions, they are capable of forming active sites which yield lower isotacticity polymer. Therefore, these additives are preferably used in 5 to 50 mole % based on $TiCl_3$ in the absence of extrinsic sources of $R'AlCl_2$. 50-100 mole % should be used when added $R'AlCl_2$ plus that formed by reacting R'_2AlCl with $AlCl_3$ in the titanium component is in the overall polymerization system. The best results are obtained when the molar amount of additive is approximately equal to the molar amount of $R'AlCl_2$ produced before and during polymerization.

The alkyl groups on the aluminum compound containing 2 to 12 carbons per alkyl group all produce higher activity catalysts. However, for propylene and higher alpha

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olefins, polymer isotacticity decreases with increasing alkyl chain length. Therefore, C_2 to C_4 alkyl groups are preferred when isotactic polymers are desired.

The halide group in the aluminum components of the catalyst is preferably chloride or bromide, with chloride being most preferred.

The alkyl groups attached to the amide nitrogen are preferably attached to secondary or tertiary carbons to achieve sufficient steric hindrance. Primary alkyls are useful only when there is sufficient branching on the carbon atom beta or gamma to the nitrogen. Open chain as well as cyclic groups may be used. The most preferred groups are isopropyl, t-butyl and cyclohexyl groups.

The additives appear to be useful with any Group IVA-VIII Ziegler transition metal catalyst which produces $R'AlCl_2$ poison by reaction with aluminum alkyls. Trivalent titanium and vanadium chlorides are preferred with those having low aluminum content being most preferred. The additives also appear to be generally useful for any monomer and mixtures of monomers.

When the dialkylaluminum amide additives are used in combination with aluminum trialkyl compounds, the preferred transition metal component is supported $TiCl_3$ or $TiCl_4$ on salts such as $MgCl_2$ or hydroxychloride in which at least one Lewis base is also present. An excess of amide over the aluminum trialkyl may be used with supported $TiCl_4$ catalysts to further increase isotacticity. Thus the mole ratio of aluminum trialkyl to amide may be 1 to 50 to 50 to 1, preferably 1 to 10 to 10 to 1. The molar ratio of the trialkyl metal compound to the supported transition metal compound is 0.5 to 1 to 200 to 1 or higher, more preferably 5 to 1 to 100 to 1. Lewis bases are normally added in less than stoichiometric amounts based on the trialkyl metal cocatalyst or the nitrogen-containing metal alkyl compound, preferably 0.1 to 1 to 1 to 1. However, the hindered Lewis bases may be added in greater

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than equimolar amounts, from 0.1 to 1 up to 10:1 mole ratio, to obtain higher stereospecificity without a major loss of activity which would occur with unhindered bases.

The advantages of the catalyst system, the process for the alpha-olefin polymerization and the compositions of the mixed dimers of the present invention can be more readily appreciated by reference to the following Examples and tables.

EXAMPLE 1

A series (A-G) of polymerization runs was carried out in a 1 liter baffled resin flask fitted with an efficient reflux condenser and a high speed stirrer. In a standard procedure for propylene polymerizations, 475 ml n-heptane (< 1 ppm water) containing 10 mmole Et_2AlCl (1.20 g) was charted to the reactor under dry N_2 heated to reaction temperature (65°C) and saturated with pure propylene at 765 mm pressure. The $TiCl_3$ (1.00 g) (6.5 mmole) was charged to a catalyst tube containing a stopcock and a rubber septum cap. Polymerization started when the $TiCl_3$ was rinsed into the reactor with 25 ml n-heptane from a syringe. Propylene feed rate was adjusted to maintain an exit gas rate of 200-500 cc/min at a pressure of 765 mm. After one hour at temperature and pressure, the reactor slurry was poured into one liter isopropyl alcohol, stirred 2-4 hours, filtered, washed with alcohol and vacuum dried.

The $TiCl_3$ was prepared by reduction of $TiCl_4$ with Et_2AlCl followed by treatment with diisopentyl ether and $TiCl_4$ under controlled conditions, yielding a high surface area delta $TiCl_3$ having low aluminum content (hereinafter "low aluminum" $TiCl_3$).

In Runs B-E, the diethyl aluminum diisopropylamide ($Et_2AlN(iPr)_2$) was added to the reactor together with the Et_2AlCl. The results summarized in Table I following show that activity increased sharply up to 1 mmole amide, then more slowly up to 3 mmoles amide. The percent heptane in-

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solubles (also called isotacticity index) remained essentially constant, then decreased slightly at 3 mmoles amide.

Runs F and G show that still larger increases in activity are obtained by premixing the $TiCl_3$ with either the amide or the Et_2AlCl.

Thus, the addition of only 5-30 mole % amide based on Et_2AlCl, or about 7-50 mole % based on $TiCl_3$, resulted in 25-250 percent increase in polymerization rate over Control Run A.

The increased activity was not due simply to higher dialkyl aluminum concentration because 13 mmoles Et_2AlCl gave only 34.1 activity.

TABLE I

PROPYLENE POLYMERIZATION
$Et_2AlN(iPr)_2$ Additive

Run	$Et_2AlN(iPr)_2$ Mmoles	Rate g/g $TiCl_3$/hr	% Heptane Insolubles(a)
A(Control)	0	34.2	95.7
B	0.5	48.2	94.7
C	1	52.2	93.3
D	2	51.8	94.9
E	3	54.2	92.0
F	2(b)	65.2	94.6
G	3(c)	83.2	91.7

(a) Insoluble in boiling n-heptane based on total product, including alcohol-solubles minus catalyst.

(b) Mixed $TiCl_3$ + amide in 12 ml n-heptane, 50°C. 15 min. before charging to reactor containing the Et_2AlCl.

(c) Mixed $TiCl_3$ + Et_2AlCl in 10 ml n-heptane, 25°C. 30 min. before charging to reactor containing the $Et_2AlN(iPr)_2$.

The results as shown by the above data are that the technique of the invention can be used to more than double activity without a significant decrease in the heptane solubles of the resulting polymer.

EXAMPLE II

The procedure of Example I was repeated for additional Runs H-N except that diethyl aluminum dicyclohexyl-

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amide ($E_2AlN(cyC_6)_2$ was used instead of the diisopropylamide. Commercial delta cocrystallized $TiCl_3 \cdot 0.33\ AlCl_3$ (Stauffer AA grade) (1.00 g) (5 mmoles) was used instead of $TiCl_3$. (This commercial $TiCl_3$ catalyst has lower activity than the "low-aluminum $TiCl_3$ catalyst" used in Example I). By "cocrystallized" it is meant that the $AlCl_3$ is an integral part of the crystal lattice of the $TiCl_3$. The results are summarized as follows in Table II.

TABLE II

PROPYLENE POLYMERIZATION
$Et_2AlN(cyC_6)_2$ Additive

Run	$EtAlN(cyC_6)_2$ Mmoles	Rate g/g $TiCl_3$ AA/hr	% Heptane Insolubles(a)
H(Control)	0	20.9	93.7
I	0.30	23.7	94.0
J	0.625	28.5	93.8
K	2	36.8	89.9
L	3	40.0	84.7
M	2(b)	32.3	93.0
N	2(c)	30.9	94.0

(a) Same as (a) in Table I.

(b) Premixed $TiCl_3 \cdot 0.33\ AlCl_3$ + amide in 10 ml n-heptane, 25°C, 30 min. before charging to reactor containing the Et_2AlCl.

(c) Premixed $TiCl_3 \cdot 0.33\ AlCl_3$ + Et_2AlCl in 5 ml n-heptane, 25°C, 30 min. before charging to reactor containing the $Et_2AlN(cyC_6)_2$.

The results in Table II show that activity nearly doubled upon addition of 3 mmoles amide (60 mole % on $TiCl_3$). In contrast to the results in Example I using an essentially aluminum-free $TiCl_3$, the polypropylene isotacticity decreased substantially with increasing amounts of amide, but at least a 40% increase of activity could be obtained without loss of isotacticity.

Runs M and N show that premixing either the amide or the Et_2AlCl with $TiCl_3 \cdot 0.33\ AlCl_3$ resulted in a smaller activity increase than was obtained without premixing (Run K), but the heptane insolubles were raised back up to the Control

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(Run H). Thus, with premixing an approximately 60% increase in activity could be obtained without loss of isotacticity.

EXAMPLE III

The procedure of Example II, Run K, was repeated except that 2 mmoles diethyl aluminum diethylamide was added instead of dicyclohexylamide. Polymerization rate was 24.9 g/g $TiCl_3 \cdot 0.33\ AlCl_3$/hr and heptane insolubles was 94.1 percent. Therefore, the unhindered diethylamide was much less effective than the hindered dicyclohexylamide in increasing catalyst activity.

EXAMPLE IV

The procedure of Example I, Runs B and D, was repeated using diethyl aluminum dicyclohexylamide with similar results (40.3 and 47.6 g/g $TiCl_3$/hr vs 34.2 for the Control).

EXAMPLE V

The procedure of Example I, Run E was followed except that brown $TiCl_3$ (most beta) was used (prepared by mixing Et_2AlCl + $TiCl_4$ in n-hexane at -30°C and heating to 65°C for 1 hr, filtered, washed with n-hexane and vacuum dried). Polymerization rate increased to 41.4 g/g TiCl/hr from 18.0 for the Control run performed in the absence of $Et_2AlN(iPr)_2$.

EXAMPLE VI

A titanium catalyst supported on $MgCl_2$ was prepared by ball milling 20 g anhydrous $MgCl_2$, six ml ethylbenzoate and 3 ml methylpolysiloxane for 100 hr at room temperature. The solid was treated with an equimolar amount (based on $MgCl_2$) of 1 M $AlEt_3$ at 100°C for 1.5 hours, filtered and washed with heptane. This product was treated with excess 40% $TiCl_4$ in heptane at 65°C, 2 hours, then with 90% $TiCl_4$, 65°C, 1.5 hours, washed thoroughly with heptane and vacuum dried, yielding a brown powder containing both $TiCl_3$ and $TiCl_4$. The procedure of Example I, Runs A (Control) and D were followed except that 1 g of the supported catalyst was used in place of $TiCl_3$. Polymerization rate in the presence of amides increased to 75.7 from 21.1 in the Et_2AlCl Control. Heptane insolubles increased to 46.4 from 35.8.

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EXAMPLE VII

Polymerization runs were made in a stirred autoclave at 100 psi propylene pressure plus hydrogen for molecular weight control using pentane diluent, 60°C, 2 hours. The Control run using 10 mmoles Et_2AlCl/5 mmoles $TiCl_3 \cdot 0.33$ $AlCl_3$ (Stauffer AA grade) produced 495 g polypropylene/g $TiCl_3$. Repeating the same run but also adding 2.5 mmoles $Et_2AlN(iPr)_2$ increased catalyst efficiency to 612 g/g $TiCl_3$.

EXAMPLE VIII

Ethylene was polymerized following the procedure of Example I, Run A. During the first 25 minutes, the ethylene absorption rate decreased from 370 cc/min to 330 cc/min. At this point, 3 mmoles $Et_2AlN(iPr)_2$ in 10 ml n-heptane was added. The ethylene absorption rate gradually increased to 360 cc/min during the next 35 minutes. Thus, the rate of ethylene polymerization is also increased by the addition of a dialkylaluminum amide, but the effect is much smaller than for propylene polymerization.

EXAMPLE IX

An ethylene-propylene copolymerization was carried out in a similar manner to the procedure of Example VIII except that only 0.5 g $TiCl_3$ plus 5 mmoles Et_2AlCl was used. The monomer feed rates were set at 150 cc/min ethylene and 1350 cc/min propylene. During the first 20 minutes, the absorption rate was 550 cc/min. At this point, 1.5 mmoles $Et_2AlN(iPr)_2$ in 10 ml n-heptane was added and the absorption rate increased to 750 cc/min for the next 15 min.

EXAMPLE X

The procedure of Example I was followed for a series of Runs T'-X' and AA except that halogenated aluminum amides were used together with various alkyl aluminum compounds. The preparation of low aluminum $TiCl_3$ prepared by the technique described in Example I was used. The results are summarized as follows in Table IV.

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TABLE IV

Run	Mmoles R_nAlX_{3-n}	Mmoles $RXAlN(iPr)_2$	Relative Activity	% Heptane Insoluble
Control	10 Et_2AlCl	--	100	95.6
T'	--	5 $EtClAlN(iPr)_2$	8.2	--
U'	5 $EtAlCl_2$	5 $EtClAlN(iPr)_2$	8.7	--
V'	5 Et_2AlCl	5 $EtClAlN(iPr)_2$	155	94.0
W'	5 $Et(C_{12})AlCl$	5 $EtClAlN(iPr)_2$	180	83.2
X'	5 $(C_{12})_2AlCl$	5 $EtClAlN(iPr)_2$	86	54.2
AA	5 $AlEt_3$	5 $EtClAlN(iPr)_2$	576	62.0
BB	10 Et_2AlCl	2 $EtClAlN(iPr)_2$	157	93.9

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The data from these experiments show the following:

(1) Aluminum amides containing less than two alkyl groups are inactive alone (Run T) or when mixed with $RAlCl_2$ (Run U), because no R_2AlCl is present for active site formation.

(2) Alkyl chloroaluminum amides increase the activity of catalysts containing R_2AlCl (Runs V', W' and BB).

(3) Long chain alkyl groups in the R_2AlCl component decrease heptane insolubles (Runs W' and X').

(4) $AlEt_3$ yields very high activity in the presence of the amide (Run AA) but heptane insolubles are substantially less than in the Et_2AlCl control.

(5) Increasing the ratio of Et_2AlCl: amide from 5:5 (Run V) to 10:2 (Run BB) gave no additional improvement in activity or heptane insolubles.

EXAMPLE XI

The procedure of Example I, Run B, was followed except that aluminum triethyl was used in combination with the diethyl aluminum diisopropylamide and the transition metal catalyst (0.2 g) was $TiCl_4$ supported on $MgCl_2$. The catalyst was made by ball milling 5 moles $MgCl_2$ with 1 mole ethyl-benzoate for one day, adding 1 mole $TiCl_4$ and milling 3 days, then treating with neat $TiCl_4$ at 80°C, 2 hours, washing with heptane and vacuum drying. The catalyst contained 3.44% Ti.

TABLE V

Run	Mmoles $AlEt_3$	Mmoles $Et_2AlNiPr_2$	Rate g/g Cat/hr	% Heptane Insolubles
Control	1	0	244	83.1
A	1	0.2	268	83.8
B	1	1	299	87.3
C	0	1	0	--
D	0.25	1	20	96.8
E	1	3	267	90.4

The amide additive increased both activity and heptane insolubles with increasing concentrations (Runs A, B and E vs. control) although the amide was inactive alone (Run C). Keeping the amide concentration constant and decreasing the

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$AlEt_3$ concentration (4 amide/1 $AlEt_3$) reduced activity but gave very high heptane insolubles (Run D vs. Run B).

EXAMPLE XII

The procedure of Example XI was followed except that t-Bu_2AlEt was used instead of $AlEt_3$.

TABLE VI

Run	Mmoles t-Bu_2AlEt	Mmoles $Et_2AlNiPr_2$	Rate g/g Cat/hr	% Heptane Insolubles
Control	1	0	248	93.8
F	1	1	265	93.8
G	1	1.2	245	94.4
H	1	1.5	258	94.5

An excess of amide over the aluminum trialkyl increased both activity and heptane insolubles over the control run.

EXAMPLE XIII

The procedure of Example XI, Runs B and E, was followed except that Et_2AlNEt_2 was used in place of $Et_2AlNiPr_2$. Polymerization rates were 230 and 246, respectively, no improvement over the control rate of 244. Heptane insolubles were 84.5 and 84.9, essentially unchanged from the control 83.1%. Comparison of these runs with Example IX, Runs B and E, show that small, non-hindered alkyl groups attached to the amide nitrogen are not effective whereas bulky groups, such as isopropyl, increase both activity and stereospecificity.

EXAMPLE XIV

A new preparation of supported catalyst was used which contained 3.16% Ti.

TABLE VII

Run	Mmoles $AlEt_3$	Mmoles $Et_2AlNiPr_2$	Mmoles EB	Rate	% HI
Control	1	0	0	506	81.6
I	1	1	0	468	85.4
J	1	1	0.1	249	93.9
K	1	1	0.2	140	97.0
L	1	1.2	0.2	166	96.4
M	1	3	0.2	282	92.2

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These experiments show that small amounts of a Lewis base added to the cocatalyst system result in a major improvement in the stereospecificity while still retaining good activity.

EXAMPLE XV

The procedure of Example XIV was followed except that hindered amides and a highly hindered Lewis base were used.

TABLE VIII

Run	Mmoles $AlEt_3$	Mmoles Amide	Mmoles Amine (3)	Rate	% HI
N	0.5	1.5 A (1)	0.5	169	98.1
O	0.88	3.12 B (2)	0.88	343	98.4
P	0.64	1.36 B (2)	0.14	387	95.8

(1) A = $Et_2AlN(cyC_6H_{11})_2$

(2) B = Et_2Al-2,2,6,6-tetramethylpiperidide

(3) Amine = 2,2,6,6-tetramethylpiperidine.

Comparison with the results in Table VII shows that the combination of hindered amide and hindered amine increased both activity and stereospecificity to higher levels than were achieved with the unhindered amides and bases.

EXAMPLE XVI

The procedure of Example XV was followed except that an unhindered Lewis base (ethylbenzoate = EB) was also added together with the cocatalysts. A different preparation of supported catalyst was used which contained only 1.75% titanium.

TABLE IX

Run	Mmoles $AlEt_3$	Mmoles Amide (2)	Mmoles Amine (2)	Mmoles EB	Rate	% HI
Control	0.4(1)	0	0	0	963	49.0
Q	0.44	1.56	0.44	0.2	279	98.6

(1) 0.08 g. Catalyst

(2) B = Et_2Al-2,2,6,6-tetramethylpiperidide.

The results in Run Q show that very high stereospecificity (98.6% heptane insolubles) was obtained by the use of a dialkyl aluminum amide and two different Lewis bases

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as modifiers for the trialkyl aluminum. The results are especially striking since the control run shows that the catalyst gave very low stereospecificity (49% HI) in the absence of cocatalyst modifiers.

EXAMPLE XVII

The procedure of Example XIV, Run I, was followed except that a diarylamide, diethyl aluminum di-ortho-tolylamide, and a new preparation of the same type of supported catalyst which contained 3.38% Ti were used. The polymerization rate was 309 g/g. catalyst/hr. and the % HI = 93.4. Comparison with Example XIV control and Run I shows that the diarylamide was more effective than the diisopropylamide in increasing stereospecificity.

Since many modifications and variations of this invention may be made without departing from the spirit or scope of the invention thereof, it is not intended to limit the spirit or scope thereof to the specific examples thereof.

CLAIMS:

1. A catalyst composition which comprises a mixture of:

(a) at least one supported Group IVA to VIII transition metal halide;

(b) a trialkyl metal cocatalyst, said trialkyl metal cocatalyst having the structure R'_3Y wherein R' is a C_1 to C_{20} primary alkyl, secondary alkyl, tertiary alkyl, neopentyl alkyl, branched alkyl, naphthenic or aralkyl group and Y is aluminium, gallium or indium;

(c) a nitrogen-containing metal alkyl compound having the structure

$$R'_2YNR_2 \quad \text{or} \quad R'XYNR_2$$

wherein Y is Al, Ga or In, X is a halide and R' is a C_1 to C_{20} primary alkyl, secondary alkyl, tertiary alkyl, neopentyl alkyl, branched alkyl, naphthenic or aralkyl group and R is C_3 to C_{20} bulky alkyl, cycloalkyl, aryl or substituted aryl groups, with the proviso that the two R groups can be taken with N to form a pyrrolidyl or piperidyl and the alkyl substituted derivatives of pyrrolidyl and piperidyl, the mole ratio of said compound to said transition metal compound being from 0.5:1 to 200:1, and

(d) at least one Lewis base.

2. A composition according to claim 1 wherein Y is aluminum.

3. A composition according to either of claims 1 and 2 wherein said trialkyl metal cocatalyst is a trialkyl aluminium cocatalyst at a molar ratio of 1 to 50 to 50 to 1 based on said nitrogen containing metal alkyl compound.

4. A composition according to any one of the preceding claims wherein said nitrogen containing metal alkyl compound is diethylaluminium diisopropylamide, diethylaluminium dicyclohexylamide, diethylaluminium 2,2,6,6-tetramethylpiperidide or diethyl aluminium diorthotolyl amide.

5. A composition according to any one of the preceding claims wherein said transition metal compound is $TiCl_3$ on a support or $TiCl_4$ on a support.

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6. A composition according to any one of the preceding claims wherein said support is $MgCl_2$.

7. A composition according to any one of the preceding claims wherein said Lewis base is an amine, ester, phosphine, ether, amide, sulfoxide, phosphine oxide, phosphate, phosphite, epoxide, saturated or unsaturated heterocycle, piperidine, pyrrolidine, ketone, tetrahydrofuran, secondary or tertiary aliphatic or aromatic amine.

8. A composition according to claim 7 wherein said Lewis base is ethyl benzoate.

9. A composition according to any one of claims 1 to 6 wherein said Lewis base is hindered.

10. A composition according to any one of the preceding claims wherein said R groups are aryl.

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European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 80 30 0705

0015763

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	FR - A - 2 380 305 (EXXON) * Claims 1-5,7,8,10-13; page 4, lines 24-37; example 6; example 10, run AA; page 15, lines 14-17 *	1-8
	FR - A - 1 294 416 (EASTMAN KODAK) * Abstract 1,a-f,2a,b *	1,4,10
	FR - A - 1 123 617 (K. ZIEGLER) * Abstract 1; page 2, column 2, line 37 and following; page 3, lines 4-7; page 6, example 12 *	1,4,10
A	US - A - 3 642 746 (N. KASHIWA et al.) * Claims 1-11; column 7, lines 29-40 *	1-3,5-8

CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)

C 08 F 10/00
4/60
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TECHNICAL FIELDS SEARCHED (Int.Cl. ³)

C 08 F 10/00-10/14
110/00-110/14
210/00-210/18
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4/02

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
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O: non-written disclosure
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L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	11-06-1980	WEBER

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